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SO_2-Rock Interaction on Io: Reaction Under Highly Oxidizing Conditions

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Laboratory simulations have been carried out to test the possibility that interactions of SO_2 and silicates can produce Na-S compounds which can account for the observed surface enrichment of Na relative to Si on Io. A wide variety of silicate compositions were heated under oxidizing conditions with a $SO_2/O_2 = 1$ gas phase at a mid-level crustal temperature for Io (1123K). All experiments produced sulfate deposits on the silicate surfaces. The nature of the sulfate changed systematically with the silicate Ca/Na ratio, with mixtures of $CaSO_4$ and Na-rich sulfate formed by basaltic compositions having higher Ca/Na but only alkali-rich sulfates formed for more granitic (low Ca/Na) compositions. For crystalline albite and an albite-orthoclase eutectic glass composition, K and Al-rich sulfates were formed. Assuming that burial of SO_2 to the temperatures of our experiments is plausible on Io and that somewhat less oxidizing conditions do not qualitatively change the results, SO_2-rock interactions producing Na-rich sulfates could account for the Io surface enrichment in Na. Observations on minor elements, such as K or Ca, in the atomic cloud or in magnetospheric ion spectra could be used to identify sulfates as Io surface phases and, conceivably, even define Ionian crustal magma types. Many analyses show significant S excesses which are best interpreted as due to the presence of bisulfate (HSO_4) components, and $NaHSO_4$ deserves consideration as an Io surface mineral. The possibility of elemental S on Io can be regarded as a totally separate issue from the problem of the surface Na enrichment.

INTRODUCTION

On the basis of bulk density, Io is a rocky planet, but, quite surprisingly, Io can only have minor amounts of silicate materials in the outer millimeter of its surface. Spectra of ions in the Jovian magnetosphere reveal only O, S, and Na [e.g., *Cheng et al.*, 1986]. Rocks typically have atomic Na/Si ratios of 0.01-0.1. Upper limits on magnetospheric Si have not been published, but it is clear that Na/Si is much larger than 1. Assuming that the ions are produced by sputtering of the solid surface, Si ions should also have been observed if the surface materials were silicate, even allowing for fractionation in the ionization and acceleration processes. The properties of the famous atomic Na cloud have been extensively studied [e.g., *Cheng and Johnson*, 1989], but the nature of the Na-bearing surface phases is unknown [*Fanale et al.*, 1982; *Johnson and Burnett*, 1990]. Using laboratory simulations, we are studying the hypothesis that Na in the atomic cloud and magnetosphere arises from Na-S phases produced by high-temperature interactions of sulfur compounds with silicates.

Johnson and Burnett [1990] showed that the interaction of liquid elemental S with silicate glass at temperatures of 1100-1200 K would produce Na-sulfides, most likely Na_2S_2. The Na-sulfides could be entrained in S magmas (or dissolved at higher temperatures) and transported to the surface during S volcanism. The issue arises, however, whether elemental S is required to explain the Na-rich surface of Io. Although widely accepted by many workers [e.g., *Moses and Nash*, 1991], elemental S is not a confirmed surface constituent of Io [*Hapke*, 1989; *McEwen and Lunine*, 1989]. Consequently, it is important to test for alternative origins for Na surface compounds which do not require elemental S. SO_2 is a confirmed atmospheric and surface constituent [e.g., *Kumar and Hunten*, 1982; *Nash et al.*, 1986; *Johnson and Matson*, 1989; *Ballester et al.*, 1990; *Lellouch et al.*, 1990]. Thus, in this study, we test whether direct interaction of SO_2 with silicate materials (SO_2 alteration) can produce Na-S compounds.

The nature of SO_2-silicate interactions will depend critically on redox conditions. For terrestrial basalt compositions, the stable S phases and corresponding silicate liquid solubilities have been relatively well-studied in water-saturated experiments over a range of oxygen fugacities and temperatures [e.g., *Carroll and Rutherford*, 1985, 1987]. For conditions more reducing than the NiNiO redox buffer, reduced S predominates, both dissolved in the liquid and as FeS. Because of the presence of SO_2, only more oxidizing conditions are relevant for Io.

Thermodynamically, S and O_2 are incompatible (cf. G. R. Van Hecke and D. B. Nash, unpublished manuscript, 1984), but at Io surface temperatures thermochemical reaction rates are negligible. Several studies of the Io atmosphere [*Kumar and Hunten*, 1982; *Ingersoll et al.*, 1985; *Lellouch et al.*, 1990] have proposed that there is a sizable O_2 component, comparable to SO_2. In this paper we report SO_2 weathering experiments in the presence of O_2 gas. We recognize that an O_2 atmosphere for Io is not well-established, and, even if present, conditions at deep crustal levels would probably be more reducing, but in any case the present experiments represent an end-member study.

For conditions more oxidizing than NiNiO, *Carroll and Rutherford* [1985, 1987] found oxidized S in the liquid and $CaSO_4$ as the stable S phase, providing no evidence for Na-S phases. However, we show that when anhydrous experiments are carried out with a wider range of silicate compositions, Na-rich sulfates can be formed as well.

EXPERIMENTAL METHOD

We have focused on glasses, as opposed to crystalline phases, because glass is ubiquitous is terrestrial lava flows and thus a plausible constituent for the Io crust.

Experiments were run by exposing polished slices to oxygen and SO_2. Samples and their compositions are given on Table 1.

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TABLE 1. Starting Materials and Experiments

Name	Experiment Number[a]	Wt % Oxides Na_2O	MgO	Al_2O_3	SiO_2	CaO	K_2O	FeO	Other
Albite[b]	KS 6	11.07	0.04	19.65	67.84	0.00	0.29	0.04[c]	0.86 H_2O
AbOr[d]	KS 12A	5.7	-	18.8	66.4	-	8.7	-	0.43% Sb_2O_3
Obsidian[e]	KS 11A, KS 11B	3.80	-	12.32	76.45	0.52	4.75	1.02[c]	0.06 TiO_2, 0.06 MnO
Soda-lime[f]	KS 5, KS 4, KS 3	15	4	1	73	7	tr	tr	tr TiO_2
AbAnDi[g]	KS 12/13	9.5	1.9	19.2	64.8	4.6	-	-	
Chon[h]	KS 13A	6.39	8.11	17.31	62.56	5.51	-	-	
KAB[i]	KS 10A, KS 10B	2.26	7.23	13.8	49.94	11.40	0.52	8.58	2.71 TiO_2, 2.82 Fe_2O_3, 0.17% MnO

All starting materials are glasses except for crystalline albite; tr is trace.
[a] All experiments are at 1123° K and for 7 days, except KS 11B and KS 10B, which were for 24 and 26 days, respectively.
[b] A. Albite, Ward's Scientific Establishment, Inc. Composition from *Deer et al.* [1966, p. 324].
[c] All Fe calculated as FeO.
[d] Albite-Orthoclase eutectic composition, Corning Glass 1298, courtesy E.M. Stolper.
[e] 1340 A.D. eruption, Mono Craters, California; North Coulee obsidian, courtesy *Newman et al.* [1988].
[f] Commercial "soft glass" slides, VWR 48318-009.
[g] Albite:Anorthite:Diopside 8:1:1 glass, Corning experimental glass 608 PEM, made by L.R. Pinckney.
[h] Chondrule mesostasis composition glass, Corning experimental glass 608 PEL, made by J. Fine, courtesy R.C. Wiens.
[i] Kilauea alkali basalt, August 1971 flow, collected by D.S. Burnett, August 30, 1973; composition assumed to be that of USGS standard powder BHVO-1 [*Gladney and Roelandts*, 1988].

The Kilauea alkali basalt (KAB) contained crystals of pyroxene and plagioclase in a glassy matrix. The Mono obsidian contained small spheres of magnetite. All other samples were compositionally homogenous to the scanning electron microscope (SEM). The samples were cut into small pieces with a diamond saw and cleaned by ultrasonic agitation in reagent ethanol, soaking in hot reagent trichloroethylene, and ultrasonic agitation in spectroscopic-grade methanol. Samples were kept in air in aluminum foil cleaned by this process before encapsulation.

Materials were exposed to a $SO_2/O_2 = 1$ gas mixture generated by the thermal decomposition of $K_2S_2O_8$ (Alfa 18227, ultrapure). Each experiment used about 50 mg $K_2S_2O_8$, enough to generate about 3 atm total pressure at 1123 K. SEM analyses of the $K_2S_2O_8$ decomposition residue (presumably K_2SO_4) showed no detectable Na; thus there is no evidence that by acting as a Na getter, the K_2SO_4 has significantly affected the outcome of the alteration reactions on the silicate glasses.

In most runs, an evacuated "hourglass" silica glass capsule was used to isolate samples from residual K_2SO_4. The $K_2S_2O_8$ went into the lower part of the hourglass; the upper contained one large (5x5 mm) and one small piece of sample, plus one 5x5 mm flat piece of silica glass control. Capsules were placed in a horizontal furnace, the temperature was raised to 1123 K (850°C), and samples were kept at this temperature for 7 days before air quenching. Heating times were of the order of an hour; cooling times were minutes. Reaction rates are sufficiently slow that it is very unlikely that significant reaction occurred during the heating and cooling stages. On opening, the existence of unreacted SO_2 was confirmed by sniffing; in most cases, SO_2 was found by this technique. Long-duration runs for KAB and obsidian (Table 1) were odorless, due to complete SO_2 reaction, or, less likely, leakage due to capsule devitrification. Products were analyzed using a SEM and an energy dispersive X ray analysis system. Comparison of point versus large area Na counting rates at different current levels on a flat sample of thenardite (Na_2SO_4) indicated beam-induced Na migration losses are not important (<10%). Spot spectra were necessary in the fine-grained reaction products; but, whenever possible, analyses were made by scanning the beam over a 5x5 μm area.

Samples mounted for analysis were flat to the eye; nevertheless; because samples tended to deform or acquire undulating surfaces during heating and because reaction products did not grow as flat films, analyzed surfaces were generally not flat, so that quantitative analysis was difficult. Corrections for local tilt were made based on the absolute S counting rate compared to flat thenardite and anhydrite standards, or, preferably, by measuring the changes in X ray peak counting rates when the sample was rotated 180°. Either technique permitted an estimate of the tilt angle. Corrections for the effect of tilt were calculated based on the procedures described by *Armstrong* [1988].

RESULTS

All elemental ratios in the following discussion are given in molar proportions. Unless specifically indicated, all experiments are 1123°K, 7 days. A summary of experiment numbers is included in Table 1.

Descriptions of Run Products

SEM images of experiment KS-6 (albite) and KS12A (AbOr) showed surfaces covered with 20-50 μm silica mounds (Figure 1).

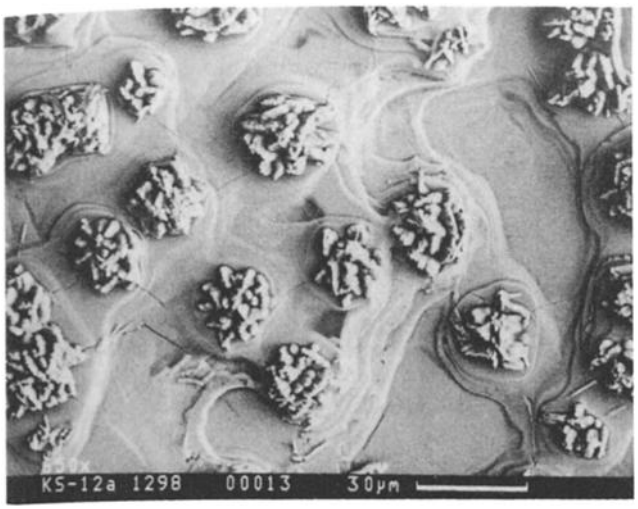

Fig. 1. SEM photomicrograph of reacted surface of experiment KS12A, AbOr composition, showing rosettes of silica, presumably crystals, sitting in a flat layer of alkali- Al-rich sulfate.

The internal structure of some mounds consisted of a crisscross pattern of vertically oriented plates. Other mounds were volcano-shaped with a raised rim and hollow interiors. The amount of reaction is less for albite than for AbOr. K, Al, Na sulfate occurs as smooth-surfaced puddles surrounding silica mounds or as isolated rough-textured regions. The K and S in the albite reaction products must come from the gas phase produced by $K_2S_2O_8$ decomposition, but the Na and Al are from the albite. The pathway for the Na to enter the sulfate could be through the gas phase, but as Al is a very refractory element, the Al in the sulfate must have been extracted from albite; thus the sulfates are reaction products not vapor deposits on an unreacted substrate. The silica mounds are presumably reaction products from the sulfate formation. For the AbOr glass (but not for albite), silica could be a devitrification product, but the mounds are not observed in control experiments in which glasses were heated in the absence of SO_2. Thus, schematically,

$$\text{albite} + SO_{3\,gas} + K_{gas} = \text{(K,Al,Na) sulfate} + SiO_2$$

with an analogous reaction for the AbOr glass. With evidence for K vapor transport, the possibility that Na has been lost to the silica glass capsule must be considered. Except for the longer obsidian experiment (11B) (discussed below) a systematic SEM check of the silica glass control samples included in all experiments showed no detectable Na. Na diffuses rapidly in silica glass [*Frischat*, 1968], so that significant loss could occur without detectable Na in the silica glass. However, Na-rich sulfates form readily in all experiments; thus there is no indication that experiments have been significantly biased by gettering of Na (or K) from the vapor phase by the silica glass capsules.

The systematic SEM examination of the silica glass controls found no element other than Si, providing additional evidence that the sulfates are reaction products rather than vapor deposits. The control silica glass from the Chon experiment was examined by photoelectron spectroscopy, which is more sensitive to surface deposits than the SEM; no S, Na, or K was found.

The surface of the KS-11A (obsidian) sample was covered in a white crust, primarily silica with only minor amounts of alkali-rich sulfate, very different from the albite and AbOr. No S phases were found in a control experiment in which powdered obsidian was heated (vacuum, 1123 K, 7 days) without SO_2 present. Because of the small amount of reaction for KS-11A (7 days), a 26-day experiment (KS-11B) was carried out. Larger amounts of sulfate were produced on the obsidian from KS11B, but also the surface of the silica glass control was coated with 1-10 μm alkali sulfate droplets. The droplets were covered with a fibrous fuzz (Figure 2) that also appears to be sulfate.

KS-5 (soda-lime) had expanded and cracked. The surface was coated with large plates of relatively pure, apparently crystalline, Na_2SO_4 immersed in rough-textured Na-rich sulfate overlying a Ca-bearing silicate surface (Figure 3). The rough-textured sulfate could be a quenched liquid. The large sulfate patches cover about 30% of the surface. The "puckered" morphology was not seen on other samples. KS-4 (soda-lime), an early run in which $K_2S_2O_8$ was mixed with soda-lime glass pieces also produced pools of Na-rich sulfate. KS-3 (soda-lime) was a mixture of millimeter-sized glass pieces and $K_2S_2O_8$ run at 923 K. At this temperature, the $K_2S_2O_8$ is incompletely broken down, with less oxygen accompanying the SO_2. Alkali-rich sulfates are seen as rims on K_2SO_4, but the amount of reaction appears much less than the 1123 K experiments. The soda-lime samples are unique in that pure SiO_2 regions are not observed on the surface.

KS-13 (AbAnDi glass) reacted heavily. The surface texture is complex, containing SiO_2 volcano structures surrounded by smooth "puddles" of Na-rich sulfate, planar growths of Na-rich sulfate (crystals?), and relatively large plates of $CaSO_4$. After initial study of the surface products, this sample was mounted in epoxy, and a cross-sectional area was exposed by grinding and polishing. The surface reaction layers that survived the sectioning process range from 15 to 50 μm in thickness and are equally complex in this view. At some points, 10-25 μm thick SiO_2 layers, the base of the volcanos, are present but are always underlain by a sulfate layer. At other points, the sulfate is thicker and goes all the way to the surface. For at least 100 μm below the reaction layers the AbAnDi glass shows major compositional

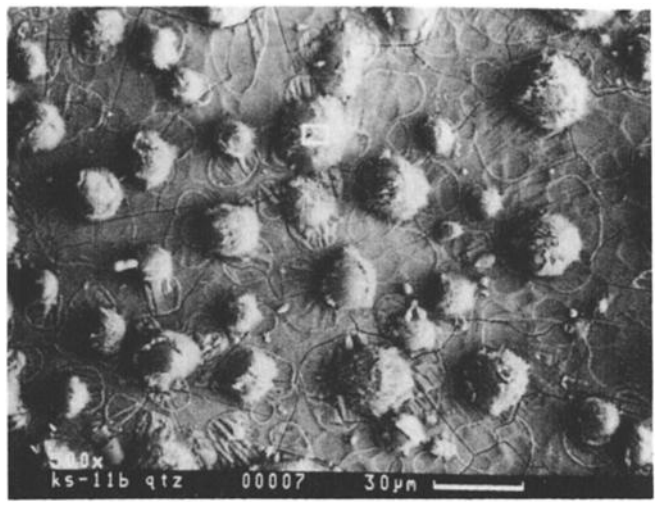

Fig. 2. SEM photomicrograph of alkali sulfate droplets on silica glass control in experiment KS11B (Mono obsidian). The fibrous material on the surface of the balls also appears to be sulfate, possibly a quench product. The droplets, which contain no Al or Ca, form from vapor phase constituents but were only observed in this experiment, presumably reflecting its longer duration. Such vapor phase sulfate deposits might form in lava tubes or during other transient silicate magma, atmospheric interactions on Io.

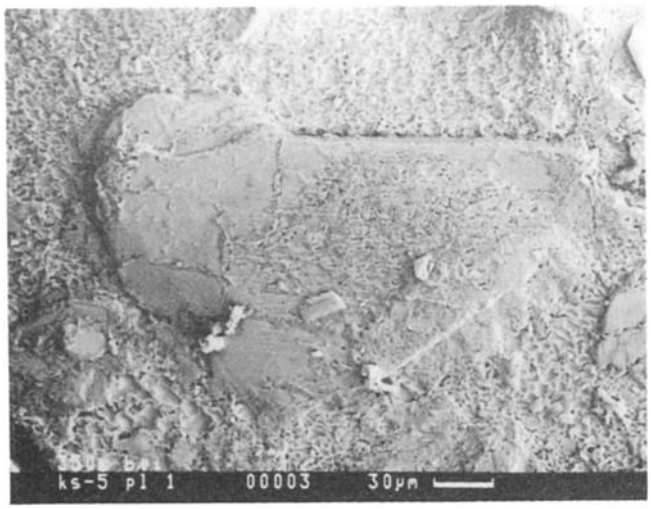

Fig. 3. Large plate (crystal?) of essentially pure Na_2SO_4 formed in experiment KS-5 (sodalime composition), sitting in a frothy matrix of similar material (quenched sulfate liquid?).

modification with depletion of Na, Mg and Ca and gains of S (up to roughly 4% SO_3) and large amounts of K (≤3% K_2O).

The surface of KS-13A (chondrule glass) contained comparable amounts of $CaSO_4$ (presumably anhydrite crystals), devitrified silica volcanoes, and a matrix of fine Na-rich sulfate crystals (Figure 4). No other cation could be detected in the anhydrite.

KS10A (KAB basalt) was heavily oxidized, with oxidation products more prominent than sulfates. Sulfur could be detected on all surfaces not coated with Fe-oxides, both rough and smooth, but the X ray spectra always indicated silicate admixtures. As Na/S counting rates were relatively high, the Na-rich sulfate is probably a thin outer surface layer, making quantitative analysis difficult Based on a few spectra, there are two sulfates, pure $CaSO_4$ and a Na-rich phase. Because of the low degree of reaction of KS10A, a second, longer (10B) experiment was carried out for 24 days. In this case no SO_2 could be smelled when the experiment was opened, so all SO_2 may have been consumed. In addition to Fe-oxides, large amounts of $CaSO_4$ formed as a surface layer. Lesser amounts of Na-rich sulfates were found as deposits on large $CaSO_4$ plates or on large recrystallized Fe-oxides, as well as in independent surface deposits.

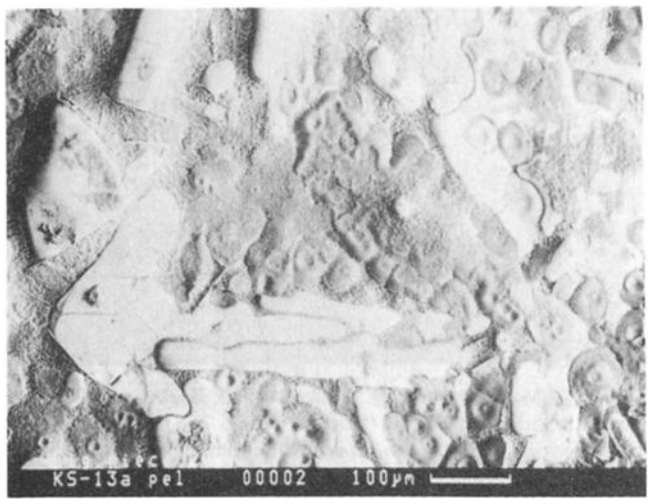

Fig. 4. Surface of experiment 13A (chondrule glass composition). Bright plates are $CaSO_4$; "volcano"-like structures are SiO_2; rough, darker matrix is Na-rich sulfate.

Summary of Sulfate Compositions

The goal of these experiments was to see if there were conditions in which SO_2-silicate reactions would produce Na_2SO_4 as a weathering product. Alkali (Na,K) sulfates were formed in all experiments, but Ca_2SO_4 was also formed for the more basaltic compositions, and for the more granitic compositions the alkali sulfates were Al-rich. In detail the compositions of the alkali-rich sulfates are highly variable, requiring graphical as opposed to tabular presentation.

Figures 5*a*-5*d* are a systematic presentation of the relative abundances of cations relative to S. The molar ratio plots are useful in evaluating possible mixtures of end member sulfate components. The high concentrations of Al were a surprise. Overall, K and Al decrease as the sulfates become more Na-rich (Figures 5*a* and 5*b*), and there is a general correlation between K and Al contents. Stoichiometric control of the alkali/Al ratios is expected. For pure $KAl(SO_4)_2$ alum, Al/S=0.5 (log Al/S=-0.3) and K/S=0.5, but only a few points (although all analyses from the AbOr composition) are close to this composition. A more general alum $[(Na,K)Al(SO_4)_2]$ would plot on the (Na+K)/S=0.5 curve (Figure 5*b*). However, as Figures 5*a* and 5*b* show, most observed compositions do not correspond to alums. For a pure "thenardite" $[(Na,K)_2SO_4]$ component, (Na+K)/S=2, but only the soda-lime products, where essentially pure Na_2SO_4 was produced, meet this expectation (Figure 5*b*). Most analyses have (Na+K)/S ratios between 0.5 and 2 (Figure 5*b*), suggesting mixtures of alum and thenardite components. Such mixtures could plausibly form as quench products of a sulfate liquid, or, alternatively, as partially equilibrated crystalline alum-thenardite solid solutions.

In general, as one proceeds from the more granitic compositions (albite, AbOr, Mono) to more basaltic (AbAnDi, Chon, KAB), Na/K ratios increase, but both K and Al decrease, so that both high Al/K (AbAnDi, Chon) and low Al/K (KAB) are observed for higher values of Na/K. Some samples have a more restricted range of compositions permitting fields to be demarcated on Figure 5 by drawing a solid line around the points. For other samples (e.g., AbAnDi or the 7-day obsidian run (KS11A)), the observed variations are almost as large as the total range of samples. It is not understood why some K-free silicate compositions form K-rich sulfates (e.g., albite) using gas phase K-species from the $K_2S_2O_8$ decomposition, while other compositions (soda-lime, Chon) form Na-rich but K-poor sulfates. There is a rather poor correlation of silicate Na_2O and sulfate Na/S, although the highest and lowest Na/S (soda-lime and AbOr) correspond to the highest and lowest silicate Na_2O. Similarly, the Al contents of the sulfates are not well-correlated with the silicate Al content.

The droplets from the long duration obsidian experiment (11B; Figure 3) have a composition consistent with a vapor condensate, with no measurable Al or Ca. They have a trace of Fe and excess S compared to (Na+K) (see below) and are most likely a $(Na,K,H)_2SO_4$ condensate.

For the basaltic compositions (Chon, KAB, AbAnDi) significant amounts of Ca and Mg are also found in the Na-rich sulfates (Figures 5*c* and 5*d*) although Ca/Na and Mg/Na are always less than 1. Only the natural rock (obsidian, KAB) compositions contain Fe, and these have small amounts of Fe in

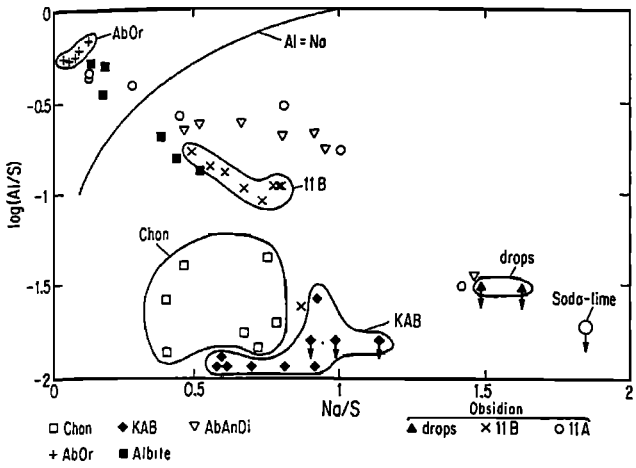

Fig. 5a. Correlation plot of Al/S versus Na/S (molar). The Al variations are so large that a log scale is required for their presentation. The curve represents compositions having equal amounts of Na and Al. The samples (from granitic silicate compositions) having Al>Na are also K-rich (compare Figure 5b). When possible, fields are drawn for analyses from a given starting silicate composition.

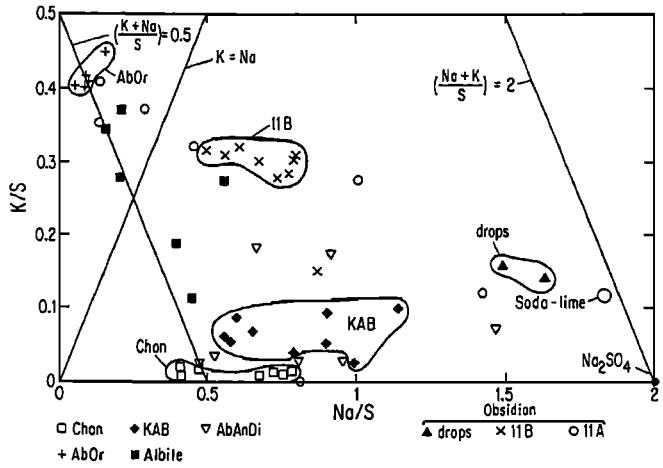

Fig. 5b. Correlation plot of K/S versus Na/S for all analyses of alkali sulfates. Although there is considerable variability, basaltic silicate compositions in general have higher Na/S and lower K/S. As shown by the distribution of points relative to the K=Na reference line, samples are found with both more and less Na than K. The (Na+K)/S=0.5 and 2 reference lines correspond to expected trends for alum $[(Na,K)Al(SO_4)_2]$ or thenardite $[(Na,K)_2SO_4]$ phases. In terms of this figure, mixtures of these components are indicated.

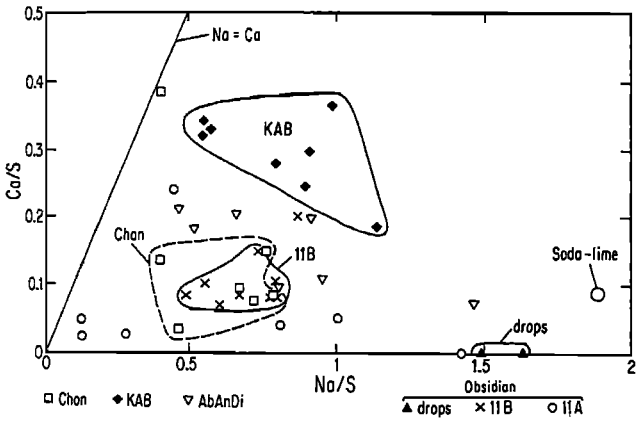

Fig. 5c. Correlation plot of Ca/S versus Na/S for Na-rich sulfates. For the basaltic compositions (AbAnDi, Chon, KAB) the Na-rich sulfate coexists with a separate $CaSO_4$ phase.

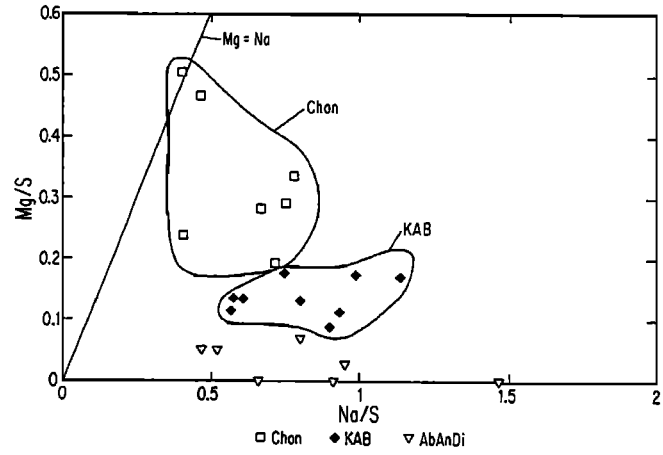

Fig. 5d. Correlation plot of Mg/S versus Na/S for Na-rich sulfates. Measurable Mg is only found for the basaltic compositions, but in some samples comparable amounts of Mg to Na are found. Basaltic compositions also have a separate $CaSO_4$ phase.

the sulfates (Fe/Na<0.2). However, only two of nine analyses of KAB Na-rich sulfates show a detectable amount of Fe. In contrast, the long-duration obsidian (KS11B) sulfates have a relatively well-defined Fe/S~0.08, over an order of magnitude higher than the KAB sulfates. This is somewhat surprising because the amount of Fe in the KAB silicate is much higher than in the obsidian sample (Table 1). Assuming that most of the oxidized Fe in KAB was ferrous, the primary Fe-bearing reaction products in the KAB experiments appear to have been magnetite and ferric oxides rather than sulfates. But in the obsidian sample, much of the Fe may have already been ferric and more readily incorporated into the sulfate as a $Fe_2(SO_4)_3$ component.

The data shown in Figure 5 suggest that the alkali-rich sulfates could represent mixtures of varying amounts of a generalized alum $[(K,Na)Al(SO)_4]$, a generalized thenardite $[(K,Na)_2SO_4]$ component, $CaSO_4$, and $MgSO_4$; however, when a quantitative description of the analyses in terms of these components is made (Figure 6), many analyses show significant S excesses, ranging up to almost a factor of 3. Analytical precision varies from point to point, but a 5% standard deviation in the S excess would be typical. Systematic errors in the correction factors, especially in the relative Na/S counting efficiencies could be up to 10%; consequently, a very conservative 20% "+2σ" error band is shown on Figure 6. There is no correlation of excess S with Al/K or Na/K with the largest excesses being in the albite and Chon experiments. It is possible that small amounts of contaminant H_2O were present; consequently, bisulfate $(Na,K,H)Al(SO_4)_2$ and $(Na,K,H)_2SO_4$ components could be present. Amelia albite is reported to have almost 1% H_2O, explaining why the albite products showed the largest S excesses. Most analyses can be satisfied by mixtures of these two components. Samples were stored in desiccators, so it does not seem possible that postexperiment hydration could produce bisulfate alteration products stable

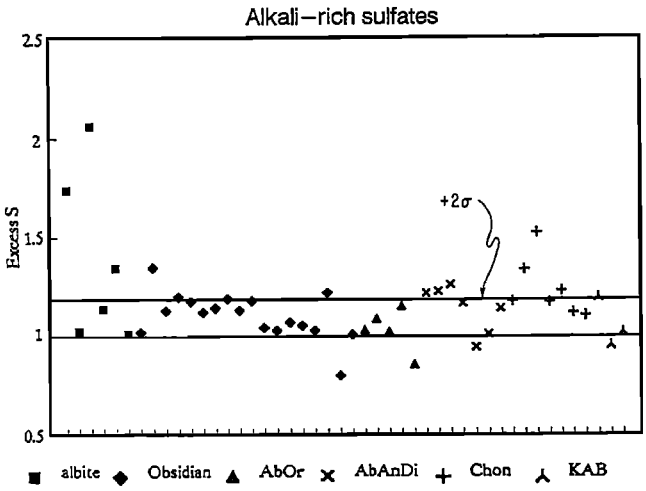

Fig. 6. Histogram of the amounts of excess S observed compared to the amount expected based on measured cation concentrations. The different silicate starting materials are distinguished. A very conservative estimate of the 2σ error limit for systematic errors still leaves many cases of analytically significant excess S. Typical 1σ estimates of random errors are about 5%. The most likely origin of the excesses is that the sulfates contain significant amounts of a bisulfate component.

in the SEM vacuum system. Alternatively, the excess S could represent a mixture of sulfates and elemental S. Elemental S would be surprising, given the highly oxidizing conditions of the experiment, but it could form as a reaction product of SO_2 with organic contaminants. Roughly 30-40 mg of organic C are required, amounts which cannot be excluded. We must also assume that the reaction rate of organic contaminants with SO_2 is much faster than with O_2 and that, once formed, the rate of oxidation of S is low. Furthermore, it is not easy to explain why independently formed elemental S and sulfate would be so intimately mixed. It may be necessary to postulate that the elemental S is soluble in an alkali-Al sulfate liquid. Overall, the presence of bisulfate components is more plausible.

Degree of Reaction

The amount of sulfate formation was highly variable among the different silicate compositions. The natural rock samples (obsidian and KAB basalt) reacted slowly; the albite and synthetic glasses showed extensive reaction. Longer-duration experiments were required to obtain sufficient amounts of reaction products for the natural rock samples (Table 1). Some unreacted surface was seen in albite and soda-lime runs. The AbOr and chondrule glass samples were completely covered by reaction products. The AbAnDi glass had undergone a change to a more K-rich composition down to 100 μm depths. The thickness of the sulfate layers on this sample corresponds to ~2-7 μm/d, a relatively high alteration rate. The alteration rate of the KAB sample is much lower, <1 μm/d.

DISCUSSION

Overview of Results

Table 2 gives a consistent organization of our results in terms of silicate Ca/Na. A major issue is the competition between $CaSO_4$ and Na-rich sulfates, and as Table 2 shows, mixtures of Na-rich sulfate and $CaSO_4$ were found for the KAB alkali basalt, chondrule glass and AbAnDi glass (highest Ca/Na). The important point is that alkali-rich sulfates formed in all experiments, although there is a progressive change in the nature of the alkali sulfate phases with Ca/Na. Relatively Na-poor, K-rich, Al-rich sulfates were formed from the AbOr and albite compositions (Ca/Na=0). The obsidian (Ca/Na=0.08) shows Na-rich sulfate usually with low K, low Al, and no Ca. As silicate Ca/Na increases, K and Al in the Na-rich sulfate decrease, and Ca and Mg appear. Table 2 is oversimplified in that the composition of the Na-rich sulfate is highly variable and in that there may be coexisting Na-rich sulfate crystals and liquid in many samples. It is possibly significant that at an intermediate Ca/Na (soda lime) essentially pure Na_2SO_4 was formed.

Formation of the Na-rich sulfate in the KAB basalt experiment is somewhat surprising. Only $CaSO_4$ would have been expected from the work of *Carroll and Rutherford* [1985, 1987]. Na_2SO_4 may have entered an H_2O-rich fluid phase in the Carroll and Rutherford experiments, may have been removed as a water soluble phase during polishing, or may have been overlooked as a minor phase in a set of complex reaction products. Alternatively, the silicate compositional range of Na-rich sulfate formation may shrink with decreasing oxygen fugacity. Finally, the Na-rich sulfates may be metastable phases for some compositions, but this would not change their potential significance for Io.

The mechanism of sulfate formation in our experiments probably involves gaseous SO_3. At 1123 K, with all species gases, the reaction:

$$2SO_2 + O_2 = 2SO_3 \quad (1)$$

has an equilibrium constant:

TABLE 2. Sulfate Reaction Products

Sample	Silicate Ca/Na molar	Products [a]
Albite	~0	K-Na-Al-sulfate
AbOr glass	~0	K-Al-sulfate; minor Na
Mono obsidian	0.08	Na-K-Al sulfate; trace Fe
Soda-lime glass	0.23	Na-sulfate
AbAnDi glass	0.28	two sulfates: $CaSO_4$ + Na-rich sulfate with Ca, K and Al
Chon glass	0.48	two sulfates: $CaSO_4$ + Na-Mg-Ca sulfate
KAB basalt	2.8	two sulfates: $CaSO_4$ + Na-Ca-Mg sulfate; trace K, Fe

Equimolar SO_2O_2 mixture at 1123 K.

[a] All products probably contain some bisulfate; see text.

$$K = [P(SO_3)]^2 / [P(SO_2)]^2 \times [P(O_2)] = 0.25 \quad (2)$$

where P is the partial pressure in atmospheres. For our experiments, neglecting interaction with silicates, $P(SO_2)$=1.7 atm, $P(SO_3)/P(SO_2)$=0.7, and $P(O_2)/PSO_2)$=1.4. Depletion of SO_3 by sulfate formation will drive reaction (1) to the right. The high SO_3 abundances make it almost certain that our reaction products are sulfates. Our primary characterization is chemical by SEM, but reconnaissance photoelectron spectroscopy (XPS) and infrared reflectance spectra clearly show major oxidized S peaks (XPS) and sulfate lines (IR), thus confirming that the major products are sulfates. Assuming SO_3 as the reactive agent, Na_2SO_4 can be formed from glasses:

$$Na_2O \text{ (glass)} + SO_3 = Na_2SO_4 \quad (3)$$

For the free oxide this reaction is highly favored thermodynamically; thus it is highly plausible, despite the reduction of Na_2O activity in the silicate glasses, that Na_2SO_4 formation would occur. Similar arguments can be made for the formation of $CaSO_4$ or $KAl(SO_4)_2$, but the compositions of mixed sulfates cannot be predicted from simple thermodynamics. The analog of equation (3) for crystalline albite is also favored thermodynamically, although formation of K, Al-rich sulfate from albite was observed.

Summarizing, sulfate formation is expected and occurs readily at the temperatures and redox conditions of our experiments. If the atomic Ca/Na ratio in the silicate glass is not too high (less than about 0.25), only alkali, Al-rich sulfates form. But, at higher Ca/Na, extending beyond the chondrite ratio of 1, two sulfates form: $CaSO_4$ and a Na-rich sulfate.

Implications for Io

Further experiments are needed at less oxidizing conditions to be certain, but our present results suggest that, for a wide range in silicate compositions, Na-rich sulfate formation by the interaction of SO_2 and silicates in the lower crust of Io is a possible mechanism for accounting for the Na-rich (relative to Si) surface. Several spectral studies have unsuccessfully searched for Na_2SO_4 on Io; however, quantitatively, up to 20% surface Na_2SO_4 coverage cannot be ruled out [*Howell et al.*, 1989].

Many of our sulfates have excess S beyond that expected for the cations analyzable by SEM X ray spectra (Figure 6). These excesses probably reflect bisulfate components formed from small amounts of contamination H_2O. On Io, H_2O appears to be a minor constituent but could be present in sufficient quantities such that if there is high degree of stability for alkali bisulfates, as suggested by our experiments, then Na_2HSO_4 might be an important Io surface mineral.

On Earth, igneous sulfates are rare and are always $CaSO_4$ [*Carroll and Rutherford* 1987]. Na_2SO_4 is not known as an igneous mineral, although it is found in evaporites. Fumarolic sulfates are common. But, as discussed by Carroll and Rutherford, only rarely are S abundances high enough in oxidized magmas for the sulfate solubility to be exceeded. Because of lower solubilities and higher magma Fe contents, iron sulfide globules are common in more reduced terrestrial basaltic magmas. Magmatic conditions on Io are probably different, with high S abundances throughout the Ionian crust. On Earth, in those rare situations where high Na/Ca magmas exist, formation of Na_2CO_3 may occur instead of Na_2SO_4. In this regard also, Io is probably very different, having a much higher SO_2/CO_2 ratio.

On Io, Na-rich sulfates could form as fumarolic phases or as directly-precipitated igneous minerals, as suggested by G. R. Van Hecke and D. B. Nash (unpublished manuscript, 1984). Formation as an alteration product, analogous to the way our experiments have been performed, may enable easy separation from silicates, as required by the observed Io surface chemistry. Preferential (relative to silicates) transport of sulfates could readily occur during fumarolic SO_2 eruptions.

A potentially important conclusion for Io from our experiments is that although sulfate formation occurred for all silicate compositions, pure Na_2SO_4 results only under fairly restricted conditions (limited range of silicate Ca/Na?). More typically, other cations (K, Al, Ca, Mg) are also significant. Observations or upper limits on these minor constituents, either in the atomic cloud surrounding Io or in the magnetospheric ion spectra test for the presence of Na-rich sulfates and possibly provide a means of a broad identification of Io crustal magma types, with granitic magmas contributing K and Al but with more basaltic magmas favoring Ca and Mg in addition to Na. It is premature to interpret the absence of these elements in magnetospheric ion spectra at present, as quantitative upper limits have not been published. Atomic K has been detected in the Io cloud, but there are only broad limits on K/Na (0.05-0.5 atomic; chondritic ratio 0.07 [*Trafton*, 1976; *Münch et al*, 1976]). There is a significant limit on Ca/Na (<0.03; chondritic ratio = 1 [*Trafton*, 1976]). These observations provide some constraints on the nature of Io crustal silicates. As a specific example, our obsidian experiment provides a simulation of conditions in a highly differentiated granitic crust on Io. Here, primarily Na, K, Al-rich sulfates are formed (Figures 5*a* and 5*b*). For this model the Io surface K/Na and Ca/Na ratio should be above and below chondritic, respectively, compatible with observations. On Earth, granitic continental crust has increased K/Na and decreased Ca/Na compared to the bulk earth, most likely as the result of plagioclase fractionation. It is plausible that an analogous K/Na enhancement would occur on Io, but more study is required on K/Na fractionations during sulfate and sulfide formation. In either case it is likely that a high K/Na in the atomic Io cloud would probably be strong evidence for evolved granitic magmas in the Io crust.

Because chemical reaction rates will be slow at the low (120-130 K) surface temperatures of Io, significant alteration should not occur in the near-surface regions, except in transient regimes (silicate lava tubes, silicate lava lakes, leading edges of lava flows, etc.). If O_2 is present, these transient interactions would be under oxidizing conditions at silicate magmatic temperatures (1500 K) which might be favorable for the formation of alkali sulfate vapor droplets analogous to those shown in Figure 2. Given the high resurfacing rate, prolonged high temperature SO_2-rock interactions might be possible by SO_2 burial, exposing SO_2 to silicates at sufficiently high temperatures for thermochemical reactions. Io crustal recycling has been modeled by *Kieffer* [1982]. Based on Kieffer's Figure 18.3, upon burial, solid SO_2 would liquify around 200 K forming aquifers and enter the fluid field at the critical point, 400 K, at a pressure of 100 bars. The maximum temperature reached by SO_2 depends on the crustal strength overlying the aquifer. Crustal interaction at silicate magmatic temperatures may be unlikely, but it is possible that mixtures of SO_2 and silicates could be capped by surface flows, producing supercritical SO_2 at temperatures between the critical point and silicate magmatic temperatures. Thus our experimental temperature (~1100 K) may not be unreasonably high for application to Io. In any case, our results can be used as a basis for extrapolation to lower temperature.

Conclusion

Assuming that experiments under slightly more reducing conditions would not produce qualitatively different results than the present experiments, we conclude that there are three viable hypotheses for the nature and origin of the Na compounds on the surface of Io: (1) Na_2SO_4 from SO_2-silicate interactions (this work), (2) Na-sulfides from elemental S, silicate interactions [*Johnson and Burnett*, 1990; G. R. Van Hecke and D. B. Nash, unpublished manuscript, 1984], (3) directly erupted volcanic Na [*Fanale et al.*, 1982; G. R. Van Hecke and D. B. Nash, unpublished manuscript, 1984]. Taken at face value, our present studies indicate that elemental S is not required to form Na compounds in crustal igneous interactions. Thus, the presence of Na compounds provides no constraint on elemental S, but, in turn, igneous formation of Na-S compounds is not tied to models of Io which contain elemental S. Measurements of minor constituents in the Io atomic cloud and torus are the key to resolving these alternatives.

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